Quantum-Mechanical Definition of Atoms and Chemical Bonds in Molecules

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14. ABSTRACT

The apparent impossibility of making meaningful assignments of indistinguishable electrons to particular atomic nuclei in a chemical aggregate has seemingly precluded quantum-mechanical definition of fragment atomic Hamiltonian operators in a molecule. Structural symmetry, con- formations, and isomers, as well as the electronic energies of constituent atoms and of their interactions in a molecule, are accordingly perceived as open problems in molecular quantum theory. Here we address assignments of electrons to atoms in molecules and provide corresponding definitions of atomic energies and of the chemical bonds between atoms from the perspective of representation theory. Molecular basis functions in the form of orthonormal (Eisenschitz-London) outer-products of atomic eigenstates allow assignments of electrons to particular atomic nuclei, and provide support for totally antisymmetric solutions of the Schrodinger equation. Self-adjoint atomic and atomic-interaction operators within a molecule defined in this context are shown to have Hermitian matrix representatives and physically significant expectation values in molecular eigenstates. Adiabatic (Born-Oppenheimer) molecular energies emerge naturally from this representation in the form of sums of the energies of individual atomic constituents and of their interaction energies in the absence of any additional auxiliary conditions. A nuanced description of chemical bonding is provided thereby which includes the interplay between atomic promotion and bonding energies, insightful com- mon representations of hybridization and atomic charge apportionment, measurable atomic entanglements, and other attributes revealed by calculations illustrating the formalism.

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Table of Contents

i

List of Figures

ii

1.0 Introduction

Although it is universally agreed upon that ordinary matter is made of atoms [1], the notion of an atom in a molecule has been relegated to the status of an observationally unknowable construction, or "noumenon" [2]. Quantum-mechanical calculations of the properties of individual atoms and bonds in molecules from molecular wave functions are correspondingly thought to require introduction of subjective auxiliary conditions to achieve specificity [3], giving rise to many individual preferences and alternative possibilities, rendering a unique theoretical definition of molecular structure and chemical bonding continuingly elusive [4–6]. These unresolved issues are arguably consequent of the absence of quantum-mechanical operator or matrix representatives of the atomic constituents of molecules and matter [7–9], such definition apparently not in simultaneous accordance with both the Principles of Quantum Theory [10] and Pauli's Exclusion Principle [11]. In this absence, disparate subjective physical interpretations of calculated molecular wave functions, and corresponding quantitative partitions of total electronic energies and other properties into atomic and bonding contributions, continue to be a focus of considerable attention, dating from early studies of Slater [12], Van Vleck [13], and Coulson [14]. Subjective qualitative opinions offered in this regard are also plentiful [15, 16], ranging from concurrence that atoms in molecules and bonds between them are meaningless illusions [17, 18] to acceptance of the numerous perspectives offered as profitably enriching the subject [19]. Of course, these circumstances have not prevented a plethora of variational and other quantum-mechanical calculations of total energies and other molecular properties employing familiar antisymmetric orbital-product representations of basis states [20, 21], as well as charge-density-related approaches [22, 23].

The ever-increasing abundance of *ab initio* and other molecular calculations has provided both additional impetus and the opportunity to pursue physical interpretations of atomic modifications and chemical bonding in molecules, in spite of the elusive nature of these quantities. In addition to early introduction of so-called equivalent molecular orbitals in interpretations of molecular charge densities [13, 14], additional criteria, such as extreme values of overlap populations or of orbital repulsion energies [24], can be employed in defining localized orbitals through *ex-post-facto* unitary transformations of the underlying molecular eigenfunctions. So-called quasi-atomic molecular orbitals [25, 26] and natural bonding orbitals [27] employed in diagnostic transformations of molecular eigenfunctions define plausible images of atoms and of the bonds between them in molecules. Partitioning of total and partial charge densities can also be employed in assignments of spatial regions in molecules to constituent atoms or chemical bonds, and to provide estimates of the degree to which individual atoms retain their electronic structural integrity when incorporated in a molecule [28–32]. Many additional differing approaches to physical interpretation of electronic structure calculations have been reported, including use of information-theory [33] and complexity concepts [34] in charge-density partitioning, as well as so-called orbital entanglements in complex electronic systems [35], to mention some representative examples.

1

Interest in electronic energy partitioning in molecules is already evident in Slater's early Virial-Theorem-based separation of total molecular electronic energies into kinetic and potential energy components [12] and in the quantitative comparisons of valence-bond and molecular-orbital methods of Van Vleck, who refers specifically to the interplay between atomic promotion and net bonding energies in the methane molecule [13]. Well-known Hellmann-Feynman considerations reveal the forces on individual atomic nuclei in a molecule for vibrational analysis [36] and also provide a basis for their chemical rationalizations [37]. Energy-decomposition schemes more generally introduce intuitively sensible but ultimately arbitrary fragment components or clusters to obtain quantitative energy expansions [38–45], whereas partitions of molecular one- and two-electron reduced density matrices [38], in conjunction with apportionment of spatial regions or functional spaces to define individual atoms [28–32], can provide total electronic energies expressed as sums of atomic and bonding contributions [46–52], to mention some representative examples. Recent reviews describe only a small fraction of the many preferences expressed for interpretations of calculated molecular wave functions, charge distributions, and energy partitions reported in the literature [53, 54].

Attempts to define meaningful self-adjoint operator representatives of atomic fragments in a molecule, as required of dynamical variables by the Principles of Quantum Mechanics [10], soon encounter restrictions consequent of electron indistinguishability [11], which seemingly preclude their unique fixed assignments to particular nuclei in a molecule [7–9]. Such atomic fragment operators do not commute with arbitrary aggregate electron permutations and so are apparently ill-defined in a molecular context, with Coulomb interaction terms, for example, changing from intra- to inter-atomic character upon electron permutations. As a consequence, the absence of meaningful partitioning of molecular Hamiltonian operators into sums of constituent atomic and interaction-energy component operators, and **also** of corresponding representations of atomic and interaction energies as Hermitian matrices evaluated with proper molecular wave functions in the standard manner [55], has largely confounded previous *ab-initio* quantum-mechanical atoms-in-molecules formulations [56–58].

The foregoing issues are addressed in the present report from the perspective of representation theory employing (Eisenschitz-London) spectral products of atomic eigenstates, familiar from early combined studies of covalent and van der Waals forces in molecules [59], to support molecular electronic states for the present more general purposes [60]. As described in earlier work [61], this representation transforms under a subgroup of the full symmetric group of electron permutations in a molecule [62–64], the absence of explicit inter-atomic electron permutations allow-ing assignments of designated electrons to particular nuclei. Quantum-mechanical operators for atoms in molecules are obtained in this representation with fixed unique electron assignments made in accordance with those employed in the atomic spectral functions. A formal basis for analysis in the closure limit is provided thereby, as is a basis for practical calculations of totally antisymmetric molecu-lar eigenstates in appropriately devised conventional finite subspaces [65].

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Molecular (Born-Oppenheimer) Hamiltonian matrices take particularly simple forms in the atomic spectral-product representation as sums over universal atomic and pair-interaction Hamiltonian matrices which can be calculated once and for all and retained for repeated applications [66, 67]. Total molecular energies obtained by conventional Hamiltonian matrix diagonalization are seen to take the form of sums over atomic and pairwise-interaction energies, expressed in terms of products of the universal atomic and interaction Hamiltonian matrices and the calculated molecular eigenvectors. Atomic energy distributions obtained in this way describe the extent to which individual atoms are excited and their electrons apportioned to atomic bonding partners over the entire molecular volume, whereas the pairwise-atomic interaction energies provide corresponding chemical-bonding energies between constituent atoms. Overall electron antisymmetry of molecular eigenstates is formally achieved in the development by convergence in the limit of closure, or by *ex-post-facto* enforcement in finite subspaces [66, 67].

The theoretical development employing the complete spectral-product representation in definitions of atomic and bonding energies for interacting atomic pairs is reported in Section 2, and finite subspace methods for computational implementations and applications described and illustrative calculations reported in Section 3.

Concluding remarks made in Section 4 provide a summary interpretation of the expressions derived and of the atomic promotion and bonding energies evaluated in molecular ground- and excited-state situations. Issues related to atomic entanglements in coherent dissociation of excited molecular states are discussed, and possible measurements of atomic energies in molecules on this basis are indicated employing coherent three-body photodissociation of the triatomic hydrogen molecule as an experimentally plausible representative example.

2.0 Theoretical Development

The atomic spectral-product representation is described in Section 2.1. A partitioning of the molecular Hamiltonian operator into atomic and atomic-interaction terms, made with appropriate electron assignments in Sections 2.2, is employed in evaluating its matrix representative in Section 2.3. The total electronic molecular energy, expressed in terms of atomic and bond energies as obtained directly from Hamiltonian matrix diagonalization, is reported in Section 2.4.

2.1 *Spectral-Product Representation*

Following Eisenschitz and London [59], the *orthonormal* atomic spectral-product representation employed here can be written in the form [68]

$$\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \equiv \left\{ \boldsymbol{\Phi}^{(1)}(\boldsymbol{1}:\boldsymbol{R}_1) \otimes \boldsymbol{\Phi}^{(2)}(\boldsymbol{2}:\boldsymbol{R}_2) \otimes \cdots \boldsymbol{\Phi}^{(N)}(\boldsymbol{n}:\boldsymbol{R}_N) \right\}_{\boldsymbol{o}}, \qquad (1)$$

where the row vector $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i}:\boldsymbol{R}_\alpha)$ formally contains all the electronic states of the atom $\alpha\,(=1,2,\ldots N)$ located at position $\boldsymbol{R}_\alpha$, with all electrons (n_α) on this atom designated by the vector of space and spin coordinates $\boldsymbol{i}\,(=\boldsymbol{1},\boldsymbol{2},\ldots\boldsymbol{n})$. The vectors $\boldsymbol{r}$ and $\boldsymbol{R}$ refer collectively to the coordinates of the entire set of molecular electrons (n_t) and of atomic positions (N), respectively, whereas the subscript $\boldsymbol{o}$ refers to the choice of an "odometer" ordering of the sequence of the N-atom product states obtained from the indicated tensor products $(\otimes)$ of atomic-state row vectors [60].

3

The molecular basis of Eq. (1) as written is complete in the limit of closure for descriptions of totally antisymmetric solutions of the Schrödinger equation in spite of the absence of explicit inter-atomic electron antisymmetry [59], and has been shown to not only contain the totally antisymmetric representation of molecular elec-trons only once, but to also span other irreducible representations of the symmetric group S_{n_t} [65]. Since the spectral-product basis transforms under an atomic-product subgroup $(S_{n_1} \otimes S_{n_2} \otimes \cdots S_{n_N})$ of S_{n_t} [61], the electron assignments of Eq.(1) are invariant to arbitrary permutations in this subgroup and can be regarded as permanent assignments of electrons to individual atoms in this context.

2.2 Partitioning the Molecular Hamiltonian Operator

The many-electron Coulomb Hamiltonian operator is written in accordance with the electron assignments of Eq. (1) in the partitioned form

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R}) = \sum_{\alpha=1}^{N} \hat{H}^{(\alpha)}(\boldsymbol{i}) + \sum_{\alpha=1}^{N-1}\sum_{\beta=\alpha+1}^{N} \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:R_{\alpha\beta}), \qquad (2)$$

where the atomic Hamiltonian operator for atom α

$$\hat{H}^{(\alpha)}(\boldsymbol{i}) = \sum_{i}^{n_\alpha} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i'=i+1}^{n_\alpha} \frac{e^2}{r_{ii'}} \right\} \qquad (3)$$

is symmetric in electron coordinates $\boldsymbol{i}$, and the interaction term

$$\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:R_{\alpha\beta}) = \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_{i}^{n_\alpha}\frac{Z_\beta e^2}{r_{i\beta}} - \sum_{j}^{n_\beta}\frac{Z_\alpha e^2}{r_{j\alpha}} + \sum_{i}^{n_\alpha}\sum_{j}^{n_\beta}\frac{e^2}{r_{ij}}$$

$$\equiv \hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:R_{\alpha\beta}) - \hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:R_{\alpha\beta}\to\infty) \qquad (4)$$

is written and evaluated in the form of the difference of atomic-pair operators

$$\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:R_{\alpha\beta}) = \hat{H}^{(\alpha)}(\boldsymbol{i}) + \hat{H}^{(\beta)}(\boldsymbol{j}) + \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:R_{\alpha\beta}), \qquad (5)$$

which are symmetric in electron coordinates $\boldsymbol{i} \oplus \boldsymbol{j}$, with $\boldsymbol{R}_{\alpha\beta} \equiv \boldsymbol{R}_\beta - \boldsymbol{R}_\alpha$ defining atomic-position separation vectors. Since all electron coordinates $(\boldsymbol{1},\boldsymbol{2},\ldots\boldsymbol{n})$ are assigned in accordance with the spectral-product representation of Eq. (1), the atomic $\hat{H}^{(\alpha)}(\boldsymbol{i})$ and atomic-pair $\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:R_{\alpha\beta})$ fragment Hamiltonian operators of Eqs. (3) to (5) commute with all permutations in the aforementioned atomic-product subgroup of S_{n_t}, and meaningful quantum-mechanical definitions of these self-adjoint operators are obtained in this particular representation [69].

2.3 Evaluating the Molecular Hamiltonian Matrix

Employing Eqs. (1) to (5), the matrix representative of the molecular Hamiltonian operator in the spectral-product basis is obtained in the form [60]

$$\boldsymbol{H}(\boldsymbol{R}) \equiv \langle \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}(\boldsymbol{r}:\boldsymbol{R})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle$$

$$= \sum_{\alpha=1}^{N} \boldsymbol{H}^{(\alpha)} + \sum_{\alpha=1}^{N-1}\sum_{\beta=\alpha+1}^{N} \boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}), \qquad (6)$$

4

where the atomic energy matrices are

$$\boldsymbol{H}^{(\alpha)} = \left\{ \boldsymbol{I}^{(1)} \otimes \boldsymbol{I}^{(2)} \otimes \cdots \boldsymbol{E}^{(\alpha)} \otimes \cdots \boldsymbol{I}^{(N)} \right\}_{\boldsymbol{o}} \qquad (7)$$

and the interaction-energy matrices are

$$\boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \left\{ \boldsymbol{I}^{(1)} \otimes \boldsymbol{I}^{(2)} \otimes \cdots \boldsymbol{V}_{\boldsymbol{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \otimes \cdots \boldsymbol{I}^{(N)} \right\}_{\boldsymbol{o}}. \qquad (8)$$

The unit matrices $\boldsymbol{I}^{(\alpha)}$ in Eqs. (7) and (8) arise from the orthonormality of the atomic eigenstates that form the spectral-product representation of Eq. (1), whereas the smaller-dimensioned atomic and atomic-pair matrices there,

$$\boldsymbol{E}^{(\alpha)} \equiv \langle \boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i} : \boldsymbol{R}_{\alpha}) | \hat{H}^{(\alpha)}(\boldsymbol{i}) | \boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i} : \boldsymbol{R}_{\alpha}) \rangle \qquad (9)$$

$$\boldsymbol{V}_{\boldsymbol{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle \boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) | \hat{V}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) | \boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) \rangle, \qquad (10)$$

require for their evaluation only the atomic $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i} : \boldsymbol{R}_{\alpha})$ and atomic-pair product functions $\boldsymbol{\Phi}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) = \{ \boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i} : \boldsymbol{R}_{\alpha}) \otimes \boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{j} : \boldsymbol{R}_{\beta}) \}$, with Eqs. (9) and (10) employing the self-adjoint operators of Eqs. (3) to (5) in these smaller-dimensioned representations. Faithful matrix representatives of the corresponding atomic and interaction-energy operators of Section 2.2 are obtained in this way which are universal computational invariants in the spectral-product basis, whereas the ordering symbol in Eqs. (7) and (8) brings these atomic and interaction-energy matrices into canonical forms prior to their summation in Eq. (6) [65].

2.4 *Partitioned Molecular Energy Expression*

The molecular energies and Schrödinger eigenstates corresponding to the Hamiltonian matrix of Eq. (6) are obtained from the diagonalization [70]

$$\boldsymbol{E}(\boldsymbol{R}) \equiv \boldsymbol{U_H}^{\dagger}(\boldsymbol{R}) \cdot \boldsymbol{H}(\boldsymbol{R}) \cdot \boldsymbol{U_H}(\boldsymbol{R}), \qquad (11a)$$

where the columns of $\boldsymbol{U_H}(\boldsymbol{R})$ contain the eigenvectors which provide the molecular eigenstates in the spectral-product basis; $\boldsymbol{\Psi}(\boldsymbol{r} : \boldsymbol{R}) \equiv \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \boldsymbol{U_H}(\boldsymbol{R})$. Employing Eq. (6), an *a priori* partitioning of the total energy is obtained in the form

$$\boldsymbol{E}(\boldsymbol{R}) = \sum_{\alpha=1}^{N} \boldsymbol{E}^{(\alpha)}(\boldsymbol{R}) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}) \qquad (11b)$$

where

$$\boldsymbol{E}^{(\alpha)}(\boldsymbol{R}) \equiv \boldsymbol{U_H}^{\dagger}(\boldsymbol{R}) \cdot \boldsymbol{H}^{(\alpha)} \cdot \boldsymbol{U_H}(\boldsymbol{R}) \qquad (12)$$

is the atomic energy matrix for an atom α in a molecule, and

$$\boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}) \equiv \boldsymbol{U_H}^{\dagger}(\boldsymbol{R}) \cdot \boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \boldsymbol{U_H}(\boldsymbol{R}) \qquad (13)$$

is the interaction-energy matrix for a pair of atoms (α, β) in a molecule.

In the limit of closure [70],

$$\hat{H}(\boldsymbol{r} : \boldsymbol{R}) \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \to \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \boldsymbol{H}(\boldsymbol{R}), \qquad (14)$$

5

the molecular energies of Eqs. (11) converge to totally antisymmetric (physical) or non-totally-antisymmetric (unphysical) Schrödinger eigenstates spanned by the spectral-product representation of Eq. (1) [71]. In this limit, the molecular Hamiltonian matrix can be blocked into separate non-interacting physical and unphysical contributions [65], as consequently are the individual atomic and atomic-pair energy matrices which sum to the total energy matrix of Eq. (11b).

Since the molecular energy matrix of Eq. (11) is diagonal by construction, the sums of the diagonal terms of the atomic and atomic-pair interaction-energy matrices of Eqs. (12) and (13) provide a partitioning of the total energies of the molecular states. The individual atomic and interaction energies on the diagonals of these matrices are weighted averages of the universal atomic $\boldsymbol{H}^{(\alpha)}$ and atomic-pair $\boldsymbol{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ Hamiltonian matrices over distributions of atomic-state and atomic-pair-state virtual excitations, respectively, as determined by the eigenvector columns of the matrix $\boldsymbol{U_H}(\boldsymbol{R})$. Accordingly, the diagonal elements of the atomic- and interaction-energy matrices of Eqs. (12) and (13) are seen to provide quantitative definitions of atomic- and atomic-pair interaction-energy surfaces in a molecule over the range of molecular geometries ($\boldsymbol{R}$) included in the calculations.

The off-diagonal terms of the matrices of Eqs. (12) and (13) refer to evaluations of individual atomic and interaction-energy operators between different molecular eigenstates. The sums of these off-diagonal terms vanish identically, in accordance with Eqs. (11), although the individual off-diagonal atomic and interaction-energy terms generally need not vanish at finite values of interactomic separation. These terms do vanish in the limit of large atomic separations, however, in contrast to the physically significant diagonal atomic terms of Eq. (12), consequent of the orthogonality of the individual molecular eigenstates employed in their evaluations.

3.0 Computational Implementation

Finite-subspace methods are described in Section 3.1 for calculating the atomic and interaction energies of atoms in molecules defined in the foregoing section, adopting previously reported methodology particularly suitable for these purposes. The approach is employed in calculations of the atomic and interaction energies of ground and excited molecular electronic states as reported in Section 3.2.

3.1 *Finite Spectral-Product Representations*

Computational implementations of the foregoing formal development must overcome the complicated nature of the spectrum of the Hamiltonian matrix in the spectral-product representation and the requirements of spectral closure [65]. Although elaborate methods have been developed for finite-subspace calculation in atomic spectral-product representations [61, 65–67, 72–74], a factored version of the general development is particularly suited to calculations of the molecular and fragment energies of focus here [66, 67, 74]. The approach requires for its validity only the linear independence of the *antisymmetrized* form of the chosen finite subspace [75], providing a Hamiltonian matrix identical in *appearance* to Eq. (6), atomic energy matrices as in Eq. (7), and interaction-energy matrices that depend only on the separation vectors of the individual atomic pairs, as in Eq. (8).

The finite-subspace molecular Hamiltonian matrix is [cf., Eqs. (6) to (10)]

$$\tilde{\boldsymbol{H}}(\boldsymbol{R}) \equiv \langle \tilde{\boldsymbol{\Phi}}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}(\boldsymbol{r}:\boldsymbol{R})|\tilde{\boldsymbol{\Phi}}(\boldsymbol{r}:\boldsymbol{R})\rangle$$

$$= \sum_{\alpha=1}^{N} \tilde{\boldsymbol{H}}^{(\alpha)} + \sum_{\alpha=1}^{N-1}\sum_{\beta=\alpha+1}^{N} \tilde{\boldsymbol{V}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}), \qquad (15)$$

6

in the chosen subspace $\tilde{\tilde{\boldsymbol{\Phi}}}(\boldsymbol{r} : \boldsymbol{R})$ of Eq. (1), the atomic and interaction-energy matrices are finite-dimensioned versions of Eqs. (7) and (8), with $\boldsymbol{V}_{\mathbf{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ in Eq. (10) given by the finite-subspace expression [66],

$$\tilde{\boldsymbol{V}}_{\mathbf{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \tilde{\boldsymbol{U}}_{\boldsymbol{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \tilde{\boldsymbol{V}}_{\boldsymbol{S_p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \tilde{\boldsymbol{U}}_{\boldsymbol{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger}, \qquad (16)$$

where

$$\tilde{\boldsymbol{V}}_{\boldsymbol{S_p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle \tilde{\boldsymbol{\Phi}}_{\boldsymbol{S}}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})|\hat{V}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})|\tilde{\boldsymbol{\Phi}}_{\boldsymbol{S}}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})\rangle. \quad (17)$$

Equation (17) is evaluated employing an explicitly antisymmetrized orthonormal finite-subspace pair representation $\tilde{\boldsymbol{\Phi}}_{\boldsymbol{S}}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})$, with the unitary matrix $\tilde{\boldsymbol{U}}_{\boldsymbol{p}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ in Eq. (16) employed to transform from this pair representation to the corresponding finite subspace $\tilde{\tilde{\boldsymbol{\Phi}}}(\boldsymbol{r} : \boldsymbol{R})$ [66]. In more general variants of the development [72–74], the form of Eq. (15) is retained but the atomic- and interaction-energy matrices there become functions of the position coordinates $(\boldsymbol{R})$ of all the atoms in the molecule. Since the condition for validity of Eqs. (15) to (17) for calculations of energies requires only the familiar linear independence of the totally antisymmetrized form of the finite spectral-product representation employed [75], the calculations reported here are indentical with those obtained from the more general computational approach under these conditions [72–74].

Energy expressions corresponding to those of Eqs. (11) to (13) are obtained employing Eqs. (15) to (17) and the finite-subspace unitary matrix $\tilde{\boldsymbol{U}}_{\boldsymbol{H}}(\boldsymbol{R})$ that diagonalizes the Hamiltonian matrix of Eq. (15). Individual energy terms $\tilde{E}_{i}^{(\alpha)}(\boldsymbol{R})$ for atoms (α) in particular molecular eigenstates (i) are provided by the diagonal entries of the atomic energy matrices $\tilde{\boldsymbol{E}}^{(\alpha)}(\boldsymbol{R})$ in the form [cf., Eq. (12)]

$$\tilde{E}_{i}^{(\alpha)}(\boldsymbol{R}) \equiv \{\tilde{\boldsymbol{E}}^{(\alpha)}(\boldsymbol{R})\}_{ii} = \sum_{k=1}^{N_{sp}} \{\tilde{\boldsymbol{H}}^{(\alpha)}\}_{kk} \, |\{\tilde{\boldsymbol{U}}_{\boldsymbol{H}}(\boldsymbol{R})\}_{ki}|^{2}$$

$$= \sum_{k=1}^{N_{\alpha}} \tilde{E}_{k}^{(\alpha)} \, |\{\tilde{\boldsymbol{U}}_{\boldsymbol{H}}^{(\alpha)}(\boldsymbol{R})\}_{ki}|^{2}, \qquad (18)$$

where Eqs. (4), (8), and (16) have been employed in the last line, $\tilde{\boldsymbol{V}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ has been replaced there by the indicated diatomic energy functions $\tilde{E}_{k}^{(\alpha\beta)}(R_{\alpha\beta})$ and the atomic energies of Eq. (18), and $\tilde{\boldsymbol{U}}_{\boldsymbol{H}}^{(\alpha,\beta)}(\boldsymbol{R})$ is the "two-atom" reduced density matrix for the atoms α and β derived from the product $\tilde{\boldsymbol{U}}_{\boldsymbol{H}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \tilde{\boldsymbol{U}}_{\boldsymbol{H}}(\boldsymbol{R})$. Here, the matrix $\tilde{\boldsymbol{U}}_{\boldsymbol{H}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger}$ is obtained from diagonalization of the atomic-pair matrix representative of Eq. (16) in the indicated finite subspace spectral-product basis to accommodate this change of representation [66, 67, 74].

The total electronic energy obtained from the foregoing expressions for a particular molecular eigenstate (i) is seen to be a sum of atomic energies for the constituent atoms and a sum of atomic-pair bonding energies of the form [cf., Eq.(11b)]

$$\tilde{E}_i(\boldsymbol{R}) = \sum_{\alpha=1}^{N} \tilde{E}_i^{(\alpha)}(\boldsymbol{R}) + \sum_{\alpha=1}^{N-1} \sum_{\beta=\alpha+1}^{N} \tilde{V}_i^{(\alpha,\beta)}(\boldsymbol{R}). \qquad (20)$$

The atomic and interaction terms given explicitly by Eqs. (18) and (19) are seen to be averages of the undisturbed atomic energies and diatomic pair-interaction energies, respectively, with the perturbing effects of the aggregate environment included through the weightings provided by the individual columns of the indicated one- and two-atom reduced density matrices.
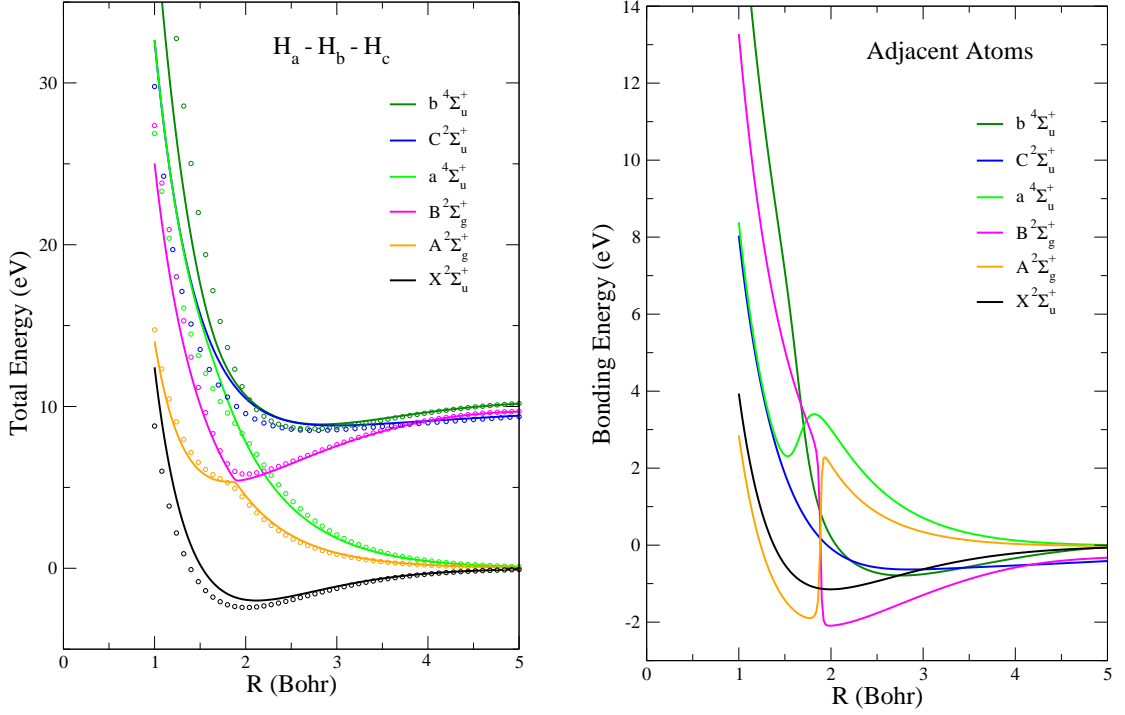
(a) Total electronic energy curves for H_3 in symmetric collinear arrangement (H_a-H_b-H_c) calculated in $1s, 2s$ atomic representations (solid lines) in comparison with valence-bond results (points), with E_{1s} set to zero.

(b) Net chemical bonding energy curves between adjacent atoms (a-b and b-c) in symmetric collinear H_3 (H_a-H_b-H_c), corresponding to the total electronic energy curves shown in Figure 1(a).

Figure 1. (*a*) Total Electronic Energy Curves and (*b*) Bonding Energies for Adjacent Atoms in the H_3 Molecule

3.2   *Illustrative Calculations*

Illustrative calculations are provided of the atomic- and bond-energies obtained from the spectral-product formalism, which provides an objective decomposition of total molecular electronic energies. In Figure 1(*a*) are shown potential energy curves for low-lying states of the H_3 molecule in symmetric collinear arrangement (H_a-H_b-H_c), calculated employing $1s$ and $2s$ atomic hydrogen spin-orbital eigenfunctions in four-term representations for each atom, in comparison with conventional valence-bond values in this basis [76]. In this classic case of three hydrogen atoms, the orthonormal atomic-product representation is closely related to the non-orthogonal valence-bond representation, but does not include the explicit overall antisymmetry of the latter. Although larger atomic representations would provide more accurate results [77, 78], the purpose of the present calculations is to make clear in a simple manner the nature of the definitions of the energies of atoms and bonds in molecules provided by the present study, rather than to report highly accurate potential curves for the H_3 molecule obtained in complicated representations.

8

The spectral-product results are evidently in good but not precise accord with the conventional valence-bond values for the six total electronic energy curves depicted in Figure 1(a). The lowest two of these curves at larger separation are $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states, whereas the third state is a $^4\Sigma_u^+$ state, all three curves dissociating to three ground-state hydrogen atoms. The three higher-lying states of $^2\Sigma_g^+$, $^2\Sigma_u^+$, and $^4\Sigma_u^+$ symmetry dissociate to limits having the energy of a promoted 2s hydrogen atom. There is evidently an avoided crossing between the A$^2\Sigma_g^+$ and B$^2\Sigma_g^+$ states and a weaker avoidance between the a$^4\Sigma_u^+$ and b$^4\Sigma_u^+$ states at smaller atomic separation. In spite of the simplicity of this representation of the H$_3$ molecule, the attributes of the present formalism can be clearly illustrated employing this example.
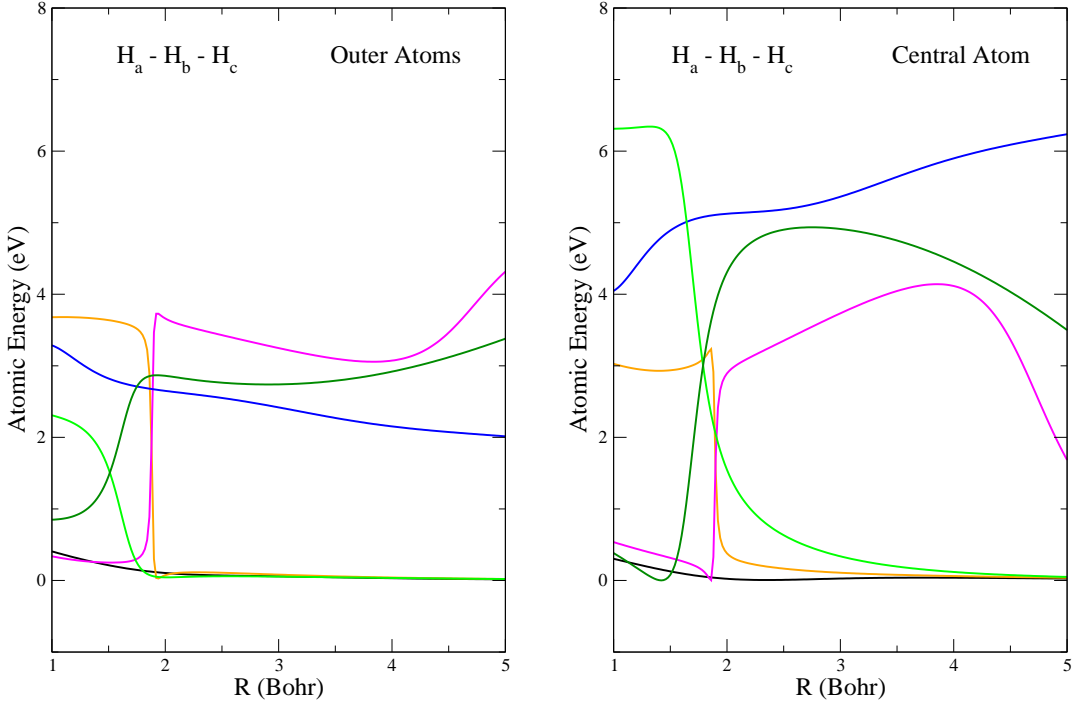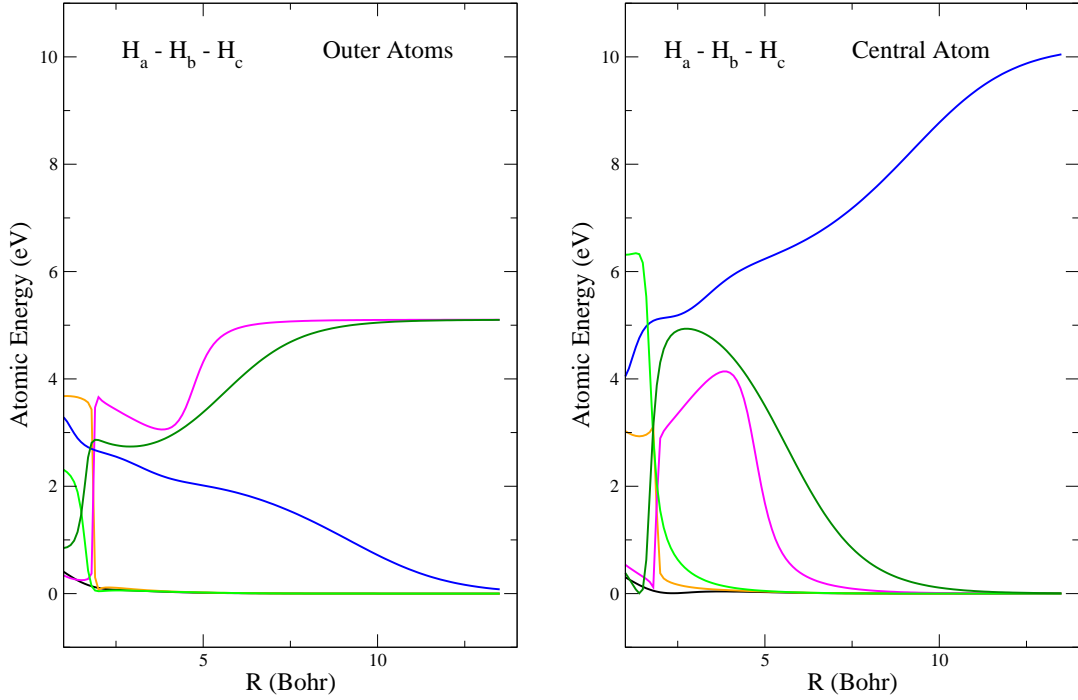

(a) Atomic energies for the outer atoms (a and c) in symmetric collinear H$_3$ (H$_a$-H$_b$-H$_c$) for the molecular eigenstates and total energy curves in Figure 1(a).

(b) Atomic energies for the central atom (b) in symmetric collinear H$_3$ (H$_a$-H$_b$-H$_c$) for the molecular eigenstates and total energy curves in Figure 1(a).

Figure 2. (a) Atomic Energies for the Two Equivalent Outer Atoms (a and c) in Symmetric Collinear H$_3$ and for (b) the Central Atom (b) in the Molecular Eigenstates and Total Energy Curves in Figure 1(a), Setting E_{1s} to Zero

In Figure 1(b) are shown the equivalent adjacent-atom (a-b and b-c) bond energies for the six states of Figure 1(a), whereas Figures 2(a) and 2(b) depict the atomic energies for the two equivalent outer (a and c) atoms and for the central (b) atom, respectively. The three atomic energies and three bonding energies for each molecular state sum to the corresponding total energy curves reported in Fig-ure 1(a), in accordance with Eq. (20). The bonding potentials between the two outer atoms (a-c) are found to show monotonic repulsive or attractive behaviors at small R in each case, but are otherwise weak and not shown here. The bond-energy curves for the two pairs of nearest-neighbor atoms in Figure 1(b) are seen to be quite different for the different molecular states, but to approach zero largely in unison at larger R, whereas the atomic energies in Figures 2(a) and 2(b) also exhibit considerably different structures, but are seen to approach limiting val-ues more slowly than the bond energies as individual atomic-energy promotion or demotion diminishes at larger R values, described in further detail below.

9

The adjacent-atom (a-b and b-c) bond energy curves for the ground $X^2\Sigma_u^+$ state (black) in Figure 1(b) are evidently similar in form to the total energy curve of Figure 1(a), with each of the two equivalent curves accounting for approximately one-half of the full energy lowering at the minimum of the potential curve. By contrast, adjacent-atom bond potentials for the $A^2\Sigma_g^+$ and $B^2\Sigma_g^+$ states (gold and magenta) in Figure 1(b) show significant changes in form as the avoided crossing is traversed adiabatically. The interchanges of 1s and 2s compositions revealed by the two curves are, of course, suggested by the avoided crossing apparent in the total energy curves of Figure 1(a) but are further quantified by the results of Figure 1(b). From a diabatic perspective, the two bonding energy curves for these states show repulsive and bound behaviors, respectively, the single pair of bond energy curves shown consequently characterizing both adiabatic and diabatic possibilities.

(a) Atomic energies for the outer atoms (a and c) in symmetric collinear H_3 (H_a-H_b-H_c) as in Figure 2(a), depicting an entangled dissociation limit.

(b) Atomic energies for the central atom (b) in symmetric collinear H_3 (H_a-H_b-H_c) as in Figure 2(b), depicting classical non-entangled dissociation limits.

Figure 3. (a) Atomic Energies for the Two Equivalent Outer Atoms (a and c) in Symmetric Collinear H_3 (H_a-H_b-H_c) and (b) for the Central Atom (b) as in Figure 2, Depicted on a Wider Scale of Atomic Separation, Setting E_{1s} to Zero

The adjacent-atom bond-energy curves for the $a^4\Sigma_u^+$ (light green) and $b^4\Sigma_u^+$ (dark green) states are seen to be largely repulsive, the former including a small barrier not discernible in the total energy curve of Figure 1(a), consequent of the weak avoidance with the latter, which is apparently less perturbed by the former. Finally, the adjacent-atom bonding potential of the higher-lying $C^2\Sigma_u^+$ state (blue) is seen to be weak, in accordance with the result of Figure 1(a).

Figures 2(a) and 2(b), with the same color scheme, show the atomic energies of the outer (a and c) and central (b) atoms, respectively, which complement the total and bond-energy curves of Figure 1(a) and 1(b), respectively. These energies are also depicted on a wider range of atomic separations in Figures 3(a) and 3(b) in order to show the asymptotic atomic energy values reached in the limit of large separation. The promotion energies of all three 1s atoms in the ground $X^2\Sigma_u^+$ state (black) are seen to be generally weak but not entirely negligible, with the central atom energy showing a small but discernible maximum at R≈4.5 Bohr in Figure

$+$

$2(b)$. The energies of the two outer atoms for the avoiding $A^2\Sigma_g^+$ and $B\,^2\Sigma_g$ states (gold and magenta) show an abrupt interchange of atomic state occupancy as the avoided crossing region is traversed adiabatically, whereas their diabatic behaviors are less extreme, as in Figure $1(b)$ for the corresponding bond energy curves. The $B\,^2\Sigma_g^+$ state (magenta) outer-atom energies approach unphysical values at larger R which are averages of the $1s$ and $2s$ atomic energies, in accordance with a coherent molecular state in which both outer atoms are symmetrically excited to entangled $1s$ and $2s$ atomic states [80, 81]. The atomic energies for the central atom in these two states show the rapid interchange in atomic state occupancy as the avoided crossing region is traversed adiabatically, with the large R limiting values in both these cases approaching the ground atomic state $1s$ energy. The large changes in atomic energy values with decreasing atomic separation in all three atoms for the $a^4\Sigma_u^+$ (light green) and $b^4\Sigma_u^+$ (dark green) states arises from the weak avoided crossing between these two repulsive states of Figure $1(a)$, as does the small barrier in the corresponding bond energy curve of Figure $1(b)$ for the former state, whereas the outer-atom energies in the latter state both approach unphysical entangled values at larger R. Finally, the central atom energy for the highest-lying $C\,^2\Sigma_u^+$ state (blue) in Figures $2(b)$ and $3(b)$ approaches the $2s$ atomic energy at large R, whereas the two outer atoms in Figures $2(a)$ and $3(a)$ approach the ground-state $1s$ energy at large R, indicating a dissociative state in which only the central atom is excited.

The atomic and bond energies reported in Figures 1 to 3 obtained employing the present atomic spectral-product formalism provide a very detailed accounting of the variation with atomic separations of these components of total electronic energy in symmetric collinear H_3. Larger representations in H_3 calculations [77, 78] provide values of atomic promotion and bonding energies which are found to converge with basis set more slowly than total molecular energies, as reported in detail elsewhere [79]. The present results nevertheless demonstrate that the atomic spectral-product development can provide a quantitative molecular electronic energy decomposition analysis free of arbitrary subjective conditions.

4.0 Discussion and Concluding Remarks

Conventional quantum-chemical calculations of the electronic structures and attributes of molecules have evolved to a remarkable degree of sophistication and abundance [20–23], enabled largely but not entirely by continuing improvements in computational hardware and software for this purpose. Considerable attention has also been directed at plausible but arguably subjective physical and chemical interpretations of the many molecular electronic wave functions, charge density distributions, and total electronic energies calculated employing such methods [53, 54]. Conceptual advances in this connection have seemingly been much less in evidence, with the continuing absence of satisfactory *a priori* quantum-mechanical definitions of atoms in molecules and of the chemical bonds between them apparently resulting in their relegation to the status of observationally unknowably constructions [2]. In the present report, adoption of a universal atomic-eigenstate-based methodology for calculating molecular energies, in an extension of early work of Eisenschitz and London [59], appears to also provide a suitable atomic-based vehicle for addressing these fundamental conceptual and interpretive issues [60].

Attention is focused in the present report specifically on quantum-mechanical definitions of operator and matrix representatives of individual atoms and of the bonds between them in molecules, and in the use thereof in obtaining a natural partitioning of the total electronic energy of a molecule into atomic and interaction energies from calculated wave functions in the absence of additional subjective conditions or definitions [3]. The expression reported here for molecular electronic energies as sums of well-defined atomic and bonding contributions provides a simple but attractive partitioning into quantities long referred to qualitatively as promotion and bond energies, with early quantitive estimates of these made in the absence of specific quantum-mechanical prescriptions or definitions [13]. Incorporation of measurable atomic and diatomic or pair-interaction energies in the formalism employs familiar universal physical fragment energies in the development, with calculated molecular eigenstates providing distributions over these quantities in the total molecular energy expression. Although these expressions might appear to apply strictly to the particular spectral-product representation employed [59, 60], it is easily seen that virtually any wave function can be transformed, with greater or lesser effort, to spectral-product form, employing, for example, considerations based on full molecular dissociation limits, in which limits atomic-product forms emerge naturally upon suitable manipulations [69, 74].

The significant differences in behaviors of the atomic and bond energies reported for the ground and excited electronic states of the collinear H_3 molecule reveal a somewhat more nuanced picture of chemical bonding than conventional electronic energy surface calculations alone suggest. Atomic-state hybridization is accommodated automatically, apportionment of electronic charge among atoms similarly takes place over the molecular volume via virtual atomic excitations, net bonding energies are balanced against positive or negative promotion energies, and entangled atomic energies are predicted by the expectation values of individual atomic Hamiltonian operators in the adiabatic dissociation limits of coherent molecular eigenstates. Such latter results, even in the simple case of symmetric collinear triatomic hydrogen reported here, are seen to be significantly more complex than the better-known cases of the entangled limits of homo-nuclear diatomic molecules [80, 81]. Since adiabatic dissociation of coherent molecular electronic states can be achieved experimentally in various ways under appropriate conditions [82–89], an ensemble of measurements of the entangled electronic energies of atomic fragments produced by the dissociation of polyatomic molecules can potentially report distributions of these for comparisons with theoretical predictions.

Although the concept of an atom in a molecule might presently be regarded as an observationally unknowable "noumenon" [2], adoption of an atomic spectral-product representation of molecular electronic structure evidently accommodates quantum-mechanical definition of self-adjoint operators that facilitate expression of molecular energies in terms of atoms and their interactions, in response to longstanding open questions in this connection and to issues raised in early study of atoms and bonds in molecules. The possibility of measuring atomic entanglements of the electronic states of atoms produced upon coherent dissociation of triatomic molecular hydrogen ($H_3 \rightarrow H + H + H$) [90–94], reported here in the symmetric collinear case, can provide a first step in measuring a property of an atom in a molecule as carried by Schrödinger entanglement into the asymptotically-large separation limit. In view of the well-known hydrogenic Coulombic degeneracy, predictions of the 2s,2p, 3s,3p,3d,... compositions of such atomic states cannot be made on basis of calculation in the large-separation limit alone and require an approach which can predict compositions of degenerate atomic states as carried from the interaction zone to asymptotic separation limits. Additional calculations of entanglement effects on coherent polyatomic dissociation over a range of dissociation symmetries, of individual atomic and bonding energies in a range of chemical situations, and of other physical properties of molecules, are in progress in further exploration of the issues raised in the present report.

12

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